

After making several forms of apparatus, in order to obviate certain difficulties of manipulation which arose and were fatal to success, I found that, when an electric current was passed between the surfaces of mutual contact of certain aqueous solutions of different specific gravities, the boundary line of contact of the two liquids became indefinite at the surface where the current passed from the lighter into the heavier solution, and became sharply defined where the current left the heavier liquid and re-entered the lighter one; and that on reversing the direction of the current several times in succession after suitable intervals of time, these effects were reversed with each such change. Also, in various cases in which the contiguous boundary layers of the two liquids had become mixed, the liquids separated, and the line of separation of the two solutions became, by the influence of the electric current, as perfect as that between strata of oil and water lying upon each other. In rarer cases two such distinct lines of stratification appeared. Other new phenomena were also observed.

As I have sought, without success, for any record of previous discovery of essentially similar effects, and as it is evident that those I have observed belong to a large class of similar phenomena, I beg leave to take the earliest opportunity of submitting this brief statement to the Royal Society.

II. "On the Critical State of Gases." By WILLIAM RAMSAY, Ph.D., Professor of Chemistry in University College, Bristol. Communicated by Professor MILLS, F.R.S. Received February 26, 1880.

In a paper read before the Chemical Society, in May, 1879, I gave an account of a method of determining what is termed by Kopp the "specific volumes" of liquids; that was shown to be the volume of liquid at its boiling-point, at ordinary atmospheric pressure, obtainable from 22,326 volumes of its gas, supposed to exist at  $0^{\circ}$ . Being desirous of extending these researches, with the view of ascertaining such relations at higher temperatures, since April, 1879, I have made numerous experiments, the results of, and deductions from which I hope to publish before long. The temperatures observed vary from the boiling-points of the liquids examined, to about  $50^{\circ}$  above their critical points; and in course of these experiments I have noticed some curious facts, which may not be unworthy of the attention of the Society.

It is well known that at temperatures above that which produces what is termed by Dr. Andrews the "critical point" of a liquid, the

substance is supposed to exist in a peculiar condition, and Dr. Andrews purposely abstained from speculating on the nature of the matter, whether it be liquid or gaseous, or in an intermediate condition, to which no name has been given. As my observations bear directly on this point, it may be advisable first to describe the experiments I have made, and then to draw the deductions which appear to follow from them.

A piece of barometer tubing, about 3 inches long, was sealed at one end and drawn into a capillary tube at the other; after being filled with methyl formate, it was exhausted, and after two-thirds of the ether had evaporated, was sealed. By this means all air was removed from the tube, which contained merely the ether and its vapour. This tube was placed in a hole, drilled in a large block of copper. The accompanying wood-cut shows its cross section. The block was placed



A, Hole for barometer-tube. B and C, Holes for thermometers.

in an inclined position, so as to slope the barometer tube to an angle of about  $30^\circ$ .

1. On applying heat the temperature of the copper gradually rose to  $221^\circ.5$  (corr.); during the rise the meniscus of the liquid gradually became less curved, and at the above-mentioned temperature disappeared. On cooling to  $218^\circ$  a mist was seen at the point where the meniscus had disappeared, and the meniscus shortly afterwards became again visible.

2. Two similar tubes were prepared, one containing less and the other more of the same ether; the point at which the meniscus disappeared in the former was  $228^\circ$ , and in the latter  $215^\circ$ .

3. A piece of barometer tubing was bent into the shape—



and heated. At  $250^\circ$  the liquid had so expanded as to fill the whole tube, although the temperature of the portion outside the heater could not have much exceeded  $100^\circ$ , for it could be freely handled. The liquid appeared in violent motion, and on cooling, before a meniscus was observed, the lower portion of the tube became filled with mist.

As soon as a meniscus was visible, the liquid boiled so violently as to give the appearance of a denser mist.



4. A tube of the shape shown was filled to the mark with methyl formate and heated in an inclined position, the portion containing the liquid being the lower. The liquid, as usual, expanded, and at the moment when the meniscus disappeared it nearly filled the lower half. The Bunsen's burner below the copper heater was then withdrawn, and on cooling, the liquid all condensed in the *lower* half.

5. The last experiment was varied by tilting the heater after the meniscus of the liquid had disappeared, so that that half which had contained the liquid was uppermost. On cooling, the liquid condensed in the *upper* half of the tube.

6. The experiment was again varied by keeping the tube at a temperature a few degrees above the point where the meniscus vanished, for half an hour. On cooling, an almost equal quantity had condensed in each division of the tube. (During Experiments 4, 5, and 6 great care must be taken to keep the heater from draughts of cold air, otherwise unequal cooling results and distillation takes place.)

7. It was noticed that that half of the tube containing liquid, after the meniscus had vanished, appeared *full*, while the other half of the tube seemed to be *empty*. The refractive indices of the fluid contained in the tubes were therefore different. The portion of the tube containing liquid was shown to be a more powerful cylindrical lens than the empty portion, for on focussing a spot behind the tube with a microscope, the focus was shorter when the portion which had contained liquid was placed between the microscope and the spot than when the portion appearing empty was interposed.

8. From experiments on the expansion of liquids above their boiling-points, of which numerical details shall be given on a future occasion, it appears probable that the specific gravity of the hot liquid, at the temperature at which the meniscus vanishes, is identical with that of the compressed gas evolved from the liquid. This has also been noticed by Ansdell in two cases, viz., hydrogen chloride and acetylene.

9. I am inclined to believe, from observations on the expansions of liquids at high temperatures, although they were not expressly directed to elucidate this point, that liquids above the temperatures at which their menisci vanish are not uniformly compressible. But as further experiments are necessary, I mention this opinion with some hesitation.

From these observations I would draw the following inferences:—

When a liquid is heated under pressure it expands, and at the same time evolves vapour. The vapour gains in specific gravity, while the specific gravity of the liquid is rapidly diminishing. *The critical point is that point at which the liquid, owing to expansion, and the gas, owing to compression, acquire the same specific gravity, and consequently mix with one another.* From the first experiment it is seen that, on cooling, the liquid contracts more rapidly than the gas, and consequently separates as a mist through the whole of the tube, and, from its gravity, separates at the lower half. The second experiment shows that when the tube contains a small amount of liquid the space left for gas is larger, and consequently more vapour must be given off by the liquid before enough gas can be compressed till it acquires the same specific gravity as the liquid; the temperature at which the meniscus disappears is consequently higher. If the space left for gas be smaller, the opposite is the case. From the third experiment it is seen that it is possible to raise the critical point of a liquid, provided a portion be continuously cooled. Probably the average temperature of the two portions of the tube is about  $220^{\circ}$ . The fourth, fifth, sixth, and seventh experiments demonstrate that by suitable means it is possible to prevent, or rather to retard, the mixing of gas and liquid. They then retain their several refractive indices. If, however, time be allowed for diffusion through the capillary tube, the whole becomes homogeneous, and the refractive indices of the fluids contained in either portion of the tube are then identical.

I shall not refer to Experiment 8 until I have made a more thorough investigation of the subject; I venture to state, however, that it looks probable that as long as gas is being compressed, pressure rises gradually with decrease of volume, whereas, even above their critical points, liquids are comparatively incompressible. I am inclined to think that carbonic anhydride, examined by Dr. Andrews, is abnormal in this respect, but of this I am by no means certain.

In conclusion, let me refer to a paper communicated to the Society by Messrs. Hannay and Hogarth last October, entitled "On the Solubility of Solids in Gases." Should the views of the subject suggested by the above experiments be correct, it follows that these gentlemen have observed nothing unusual, but merely the ordinary phenomenon of solubility of a solid in a hot liquid. This view is borne out by their own experiments. They found that on reducing pressure, that is, on allowing the liquid to change to gas, the solid precipitated; and also on heating the tube containing the solution locally, that is, by converting the liquid near the heated point into gas, precipitation took place. I have taken the liberty of repeating one of their experiments with a slight modification.

A tube shaped like that used in Experiment 4, after a small fragment of potassium iodide had been placed in the lower compartment,

was filled with nearly anhydrous alcohol: and after rather more than two-thirds of the alcohol had been evaporated under reduced pressure, the tube was sealed. The lower portion of the tube contained a strong alcoholic solution of potassium iodide, besides a small piece of undissolved salt. The upper portion of the tube was free from alcohol, but its walls were encrusted with a thin crystalline film of potassium iodide. The tube was heated in a sloping position, the liquid being in the lower half. After the meniscus had disappeared, the iodide in the lower half of the tube dissolved, while the film in the upper half, even in its thinnest portions, remained unchanged. On cooling, very sparkling crystals deposited in the lower half of the tube, but no glittering crystals in the upper half.

By repeated distillation the iodide in the upper portion of the tube was washed down into the lower half, and when dry the sides of the upper tube were quite bright and clean. The tube was again heated in the same position to  $20^{\circ}$  above the temperature at which the meniscus had disappeared. On cooling the sparkling crystals again appeared in the lower tube, but not a trace in the upper tube. To eliminate all possibility of mistake the experiment was repeated five times with the same result, and finally the alcohol was distilled into the upper tube; it was then broken off, and its contents carefully tested for iodine with sodium hypochlorite and starch-paste. There was not the faintest blue colour, and it is therefore certain that potassium iodide is absolutely insoluble in alcohol vapour.

It would be interesting to speculate on the condition of a fluid, of which two portions possess the same specific gravity, but refract light differently. Such speculations would, however, be premature in our present knowledge of the subject.

In conclusion, I may remark, that Messrs. Hannay and Hogarth found that the absorption spectrum of coloured salts remains unaltered, even when the liquid in which they are dissolved loses its meniscus. Surely no clearer proof is needed to show that the solids are not present as gases, but are simply solutions in a liquid medium.

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Since the foregoing was written, Professor Stokes has been so kind as to suggest in a letter to Dr. Mills, some possible causes of error, which may be briefly catalogued as follows:—

1. The tubes may have contained air.

That this cannot have been the case is, I think, ensured by the method by which they were filled. The tube was *completely* filled with liquid, and the liquid made to evaporate out under a vacuum of 25 inches till its volume had become reduced to the required amount. While the reduced pressure was sustained, the tube was sealed at the

base of its capillary neck. It is improbable that the liquids experimented on dissolve air, for when heated, no air-bubbles can be seen to escape.

2. The liquids may not have been quite pure; they may not have been absolutely free from water.

The methyl formate used in the experiments presents no special advantage but that of its meniscus disappearing at a comparatively low temperature. It was procured from Kahlbaum, and previous to use had been distilled over metallic sodium. Its boiling-point was absolutely constant. Still, as treatment with sodium might have led to the formation of some other compound of nearly the same boiling-point, it was redistilled, in accordance with a suggestion of Professor Stokes, and the first and last portions of the distillate were selected for experiment. Two tubes were filled to as nearly the same height as could be judged by eye, one with the first portion of the distillate and one with the last. Both were heated at the same time in the copper heater, and were exactly similarly placed with regard to the thermometer. The temperature of the heater having been raised till the meniscus had disappeared in both tubes, the source of heat was removed and the heater was allowed to cool. The tube containing the first fraction gave the first symptoms of a cloud, or mist, at  $218.4$  (corr.), and that containing the last fraction at  $218.1$  (corr.). The very slight difference is doubtless owing to the two tubes not containing exactly the same amount of liquid.

To eliminate any source of error dependent on the use of methyl formate, two other substances were employed, viz., carbon disulphide,  $\text{CS}_2$ , and carbon tetrachloride,  $\text{CCl}_4$ . The former of these liquids was rectified five times over sodium, and then boiled at  $48.7$  (corr.). The latter was rectified four times over phosphoric anhydride, and boiled constantly at  $77.5$  (corr.).

They yielded the following results:—

	Tube more than half full.		Tube less than half full.
$\text{CS}_2$ .....	282.7	.....	286.4
$\text{CCl}_4$ .....	283.3	.....	288.4

These readings are given for the first appearance of a cloud in the tube on cooling, and differ from the temperature at which the meniscus disappears by being about half a degree lower. They also do not represent extreme instances, for in the first cases the liquids do not entirely fill the tube, and in the second about half an inch of liquids remains in the tubes before it becomes impossible to distinguish liquid from gas.

3. Owing to too rapid rise of temperature, the tubes and the heater may not have been at the same temperature.

The numbers given are not the result of one reading, but the mean of four or five. The copper block, after being raised to the temperature at which the meniscus of the liquid disappeared, was allowed to cool till a cloud became visible, shortly afterwards followed by a reappearance of the meniscus. The temperature was again raised, and so on, readings being taken each time. They never differed by more than half a degree. The tubes, therefore, must have possessed the temperature of the heater.

The experiments described in a former part of this paper, relating to the difference of refraction shown by a liquid above its so-called critical point, and the gas evolved from it, were repeated with carbon tetrachloride and carbon disulphide, and held good in both cases. The phenomena observed differed in no particular from those already described.

In conclusion a few remarks on the liquefaction of the so-called permanent gases may not be deemed out of place. If the deductions from the above experiments be correct, it follows that that form of matter which we call gas may be converted into liquid by pressure alone; but the meniscus will never become visible, for the process of change is a gradual one. To render the meniscus visible, it is necessary to take advantage of the fact that liquids under such circumstances have a much greater coefficient of expansion by heat, and conversely a much greater coefficient of contraction on withdrawal of heat, than gases. It, therefore, becomes necessary to lower the temperature until the liquid by contraction acquires a specific gravity greater than that of its gas, and then, and not till then, does the phenomenon of a meniscus become observable.

### III. "Revision of the Atomic Weight of Aluminium." By J. W. MALLET, F.R.S. Received March 13, 1880.

(Abstract.)

After remarking that there is probably no one of the so-called chemical elements, equally abundant in nature with aluminium, and occurring in as numerous compounds, with regard to the atomic weight of which our knowledge has long rested upon so slender a foundation of accurate experiment, the author gives a brief statement of prior determinations, noticing in succession the researches of Berzelius, Sir Humphry Davy, Thomson, Mather, himself, Dumas, Charles Tissier, and Terreil, and quotes the numbers given in several of the more recent chemical handbooks, reports, &c.

He then proceeds to describe a redetermination of this atomic



A. Take the temperature tube B and C. Take the thermometer.





